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Dielectric Study of Binary Mixtures of Sec-Butyl Alcohol and Ethylenediamine at Microwave Frequency

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Abstract: ***In this paper the values of dielectric constant ($\in'$) and loss factor ($\in''$) have been experimentally determined for binary mixture of Secondary Butyl Alcohol +Ethylenediamine at 9.85 GHz microwave frequency at 25°C temperature. The values of $\in'$ and $\in''$ have been used to evaluate the molar polarization (P_{12}) and the excess permittivity ($\Delta\in'$, $\Delta\in''$). The excess parameters for viscosity ($\Delta\eta$), square refractive index (Δn_D^2) and activation energy (E_a) also determined for viscous flow. These parameters have been used to explain the molecular interaction and formation of complex in the mixture***.

Keywords: Dielectric constant, Dielectric loss, loss tangent, Binary mixture

1. Introduction

The study of dielectric behaviour of binary mixtures of polar molecules under varying conditions of composition has evoked considerable interest. Because when the binary mixture is formed, the viscosity, density, refractive index and dielectric parameters do not vary linearly.

The deviation of these parameters from linearity is called excess parameters. The excess parameters are more sensitive towards inter molecular interactions in the liquid mixtures and gives valuable information about dipole – dipole interaction in the liquid mixture and molecular motions.

2. Literature Survey

Several workers[1-5] have reported utility of dielectric measurement while studying the molecular interaction in a binary mixture of liquids. Sengwa[1] has made comparative dielectric study of mono, di and trihydric alcohols. He has discussed the effect of viscosity on average relaxation time of mono, di and trihydric alcohols.

Singh P. J and Sharma K S.[4] reported the formation of complexes through hydrogen bonding in some binary liquid mixers of ketone -amine using the microwave technique. Das and Hazra[3] have studied the excess properties of binary mixturesof $N-N$ dimethylacetamide with 2-ethoxyethenol and explained in terms of the interaction between unlike molecules in the mixture.

With this background the present investigation is aimed to study the dielectric behaviour of binary mixture of Sec-butyl alcohol (*SBA*) and ethylenediamine (*EDA*). This study is expected to provide useful information regarding the molecular interactions and formation of complex in the mixture.

3. Experimental Methods

Sec-Butyl alcohol (*SBA*) A.R. grade and ethylenediamine (*EDA*) A.R. grade procured from M/s S.D. Fine Chemicals and used without further purification. The two liquids according to their proportions by volume were mixed well and kept for six hours in a well stoppered bottle to ensure good thermal equilibrium. The density (ρ) and viscosity (η) of pure compound and their binary mixtures were measured using Pycknometer and Oswald's viscometer respectively. The refractive indices for sodium D-line were measured by using Abbe's refractometer

The dielectric constant ($\in'$) and dielectric loss ($\in''$) were measured by using Surber's technique[6,7] of measuring reflection coefficient from air dielectric boundary of the liquid. the microwave source Reflex Klystron is switched on. The output power from the detector of forward directional coupler is noted. This gives forward power (P_f) again the output power from the detector of reverse directional coupler is noted. This gives reverse power (P_r) (that is reflected power). The shorting plunger which is initially at the bottom of the empty dielectric cell, touching 90° bend, carefully moved up. Moving the plunger in steps, its position (X) and reflected output power (P_r) is measured. From the data obtained for empty cell, the guide wavelength (λ_g) is obtained. Now the dielectric cell is filled with the sample under taken for study by taking out the shorting plunger and then installed the plunger in the cell and moved it through the sample till it touches the 90° bend. Moving the plunger slowly up through the experimental liquid by micrometer screw, the position (X) of the plunger and corresponding output power is recorded. From the data, wavelength (λ_d) of radiation in dielectric is obtained. The experimental set up and procedure employed for measurement of dielectric constant ($\in'$) and dielectric loss ($\in''$) were same as reported by Singh and Sharma[4]

Dielectric Parameters:

Suber [6,7] has derived the following relations for dielectric parameters $D, \in', \in''$.

$$D = \tan\left[2\tan^{-1}\frac{(\alpha_d\lambda_d)}{2\pi}\right] \quad [1]$$

$$\in' = \left(\frac{\lambda_o}{\lambda_c}\right)^2 + \left(\frac{\lambda_o}{\lambda_d}\right)^2\left[1-\tan^2\left(\frac{1}{2}\tan^{-1}D\right)\right] \quad [2]$$

and $$\in'' = \frac{1}{\pi}\left(\frac{\lambda_o}{\lambda_d}\right)^2\alpha_d\lambda_d \quad [3]$$

where λ_o is free space wavelength, λ_c is cut off wavelength for the wave guide, $\alpha_d\lambda_d$ is the attenuation constant per unit length due to dielectric, 'λ_d' is the wavelength of electromagnetic waves in the wave guide filled with dielectric. Now the parameters to be measured are λ_d and $\alpha_d\lambda_d$. The dissipation factor D for the system.

The free energy of activation E_a of the viscous flow for the pure liquids and their binary mixtures is obtained by using the following equation [9]

$$\eta = \left(\frac{hN}{V}\right)\exp\left(\frac{E_a}{RT}\right) \quad [4]$$

where η is the viscosity and V is molar volume of the liquid and other symbols have their usual meaning.

The values of molar polarization of the mixtures were obtained by using the formula [9,10]

$$P_{12} = \left[\frac{(\in'-1)}{(\in'+2)}\right]\left[\frac{X_1M_1 + X_2M_2}{d}\right] \quad [5]$$

where M_1 and M_2 are the molecular weight, X_1 and X_2 are the mole fraction of the constituents of the mixture.

4. Result and Discussion

The values of viscosity (η), the square of refractive index (n_D^2), the dielectric constant ($\in'$), the loss factor ($\in''$), the tangent ($\tan\delta$), the activation energy (E_a) and molar polarization (P_{12}) with increasing mole fraction (X) of EDA are listed in table 1

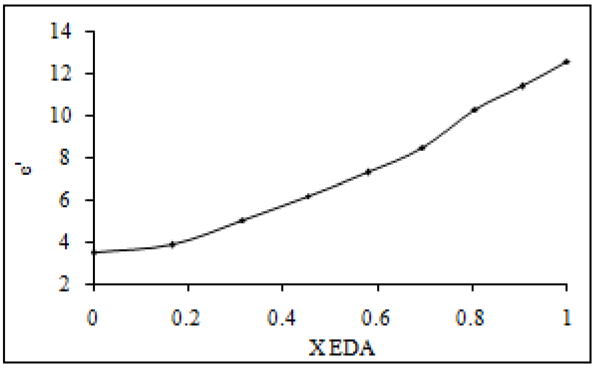

Figure 1: Variation of Dielectric Constant V/s Mole Fraction of EDA

The values of dielectric constant ($\in'$) increases with mole fraction of EDA in the mixture, indicating formation of complex in the mixture as suggested by P.Job[8]

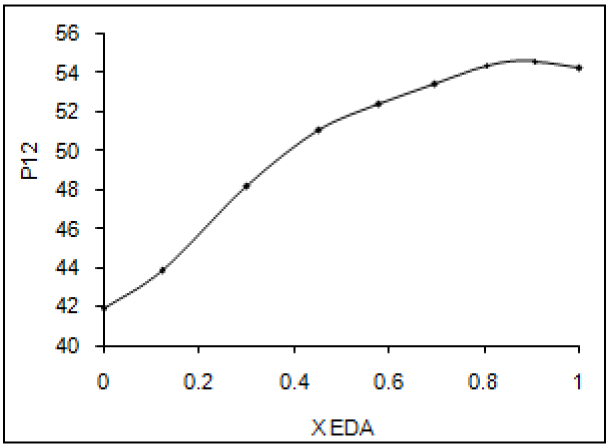

Figure 3: Variation of Molar Polarization V/s Mole Fraction of EDA

The graph of tan δ versus mole fraction of EDA shows microwave energy absorption is maximum in mixture than pure liquids. The existence of prominent maxima is at equimolar ratio of interacting solutes. An interaction causing association between two types of molecules[2].

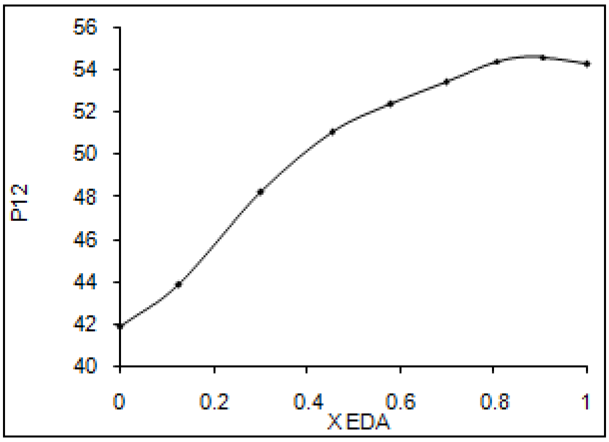

Figure 3: Variation of Molar Polarization V/s Mole Fraction of EDA

Fig.3 shows the variation of molar polarization (P12) versus mole fraction of EDA in the mixture. The intersection of straight line at X=0.5 represents the separate region of high and low concentration of EDA and can be interpreted as point of maximum concentration of complex. Similar kind of results have been predicted by Singh and Sharma [4]

Excess parameters of a binary mixture are the measure of deviation from ideal behavior of the mixture and found to be highly sensitive towards molecular interaction in the liquid mixture. The values of excess permittivity ($\varepsilon'$and ε''),excess viscosity($\Delta\eta$),excess refractive index(Δn^2_D)and excess activation energy(ΔE_a) are shown in table 2calculated using relation[4]

Where ΔY is any excess parameter and Y refers to above-mentioned quantity. The subscript m, 1 and 2 in above equation are respectively for mixture, component 1 and component 2. X_1 and X_2 are the mole fractions of the two components in the liquid.

All five excess parameters show deviation in the binary mixture from linearity, indicating interaction between SBA and EDA molecules and complex formation is found to be at equimolar ratio of mole fraction of EDA.

5. Conclusion

The values of dielectric constant ($\in'$), loss tangent ($\tan\delta$), molar polarization (P_{12}) and excess parameters have been reported for *SBA+EDA* binary mixture at various concentration of *EDA*.

1) Tan δ curve suggest that the absorption in the mixture is greater than pure compounds.
2) The non-linear behavior of dielectric constant versus mole fraction of *EDA* suggests formation of complex in the mixture.
3) The molar polarization curve suggests the 1:1 type complex formation in the mixture taking place.
4) Deviation of excess parameters from linearity suggests solute-solute interaction in the mixture.

6. Future Scope

1) Dielectric parameters are useful to study molecular interaction in binary or ternary mixtures.
2) Same binary mixtures can be studied using ultrasonic techniques

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Table 1: Values of mole fraction (X) of EDA, density (ρ), viscosity (η), square of refractive index (n_D^2), dielectric constant ($\in'$), loss factor ($\in''$), loss tangent ($\tan\delta$), activation energy (E_a) and molar polarization (P_{12}) for binary liquid system of (EDA + SBA) at 25°C

X	ρ	η (cp)	n_D^2	$\in'$	$\in''$	$\tan\delta$	E_a Kcal/mole	P_{12}
0.0000	0.8013	1.9273	1.9656	3.483	0.0573	0.0164	3.436	41.890
0.1644	0.8158	1.9096	1.9909	3.870	0.7427	0.1918	3.430	43.042
0.3146	0.8311	1.7997	2.0192	5.055	1.5410	0.3049	3.395	48.212
0.4524	0.8416	1.6983	2.0392	6.191	2.1530	0.3478	3.358	51.038
0.5793	0.8524	1.5052	2.0564	7.284	2.3590	0.3238	3.289	52.406
0.6965	0.8628	1.4035	2.0794	8.493	2.4610	0.2898	3.248	53.264
0.8051	0.8726	1.3160	2.1054	10.321	2.5390	0.2461	3.209	54.423
0.9060	0.8828	1.2289	2.1199	11.421	2.430	0.2127	3.169	54.629
1.0000	0.8894	1.0796	2.1316	12.602	1.0070	0.0799	3.126	53.690

Table 2: Values of excess parameters $\Delta \in'$, $\Delta \in''$, $\Delta\eta$, Δn_D^2 and ΔE_a along with mole fraction (X) of EDA for the binary liquid system of SBA+EDA at 25°C.

X	$\Delta \in'$	$\Delta \in''$	$\Delta\eta$	Δn_D^2	ΔE_a
0.1644	-1.1080	0.5363	0.1170	-0.00293	0.04870
0.3146	-1.2890	1.1989	0.1304	-0.00342	0.06290
0.4524	-1.4070	1.6852	0.1361	-0.00416	0.07135
0.5793	-1.4681	1.7762	0.0530	-0.00879	0.04385
0.6965	-1.3243	1.7702	0.0475	-0.00593	0.04099
0.8051	-0.4844	1.7519	0.0490	-0.00145	0.03851
0.9060	-0.3027	1.5509	0.0447	-0.00135	0.03105